

Conference Paper

The Research of the Carbothermic Solid–Phase Red Mud Reduction Process in the Presence of Sodium Sulphate

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Abstract

Russia has accumulated about 600 million tons of the red mud that is alumina production waste generated by Bayer method, but currently only a small amount of the total accumulated red mud is recycled. Solid–phase carbothermic reduction of red mud in the presence of sodium salts with magnetic separation can be a promising method for iron extraction. In this paper, the effect of the addition of sodium sulphate on the reduction of iron–containing phases and the growth of iron grains during solid–phase carbothermic reduction of red mud was investigated. The results show that 10% sodium sulphate additive significantly accelerate the growth of reduced iron grains, but decrease the degree of its reduction at temperatures above 1100°C. The explanation of mechanism of sodium sulphate effect on the iron grain growth was proposed. Optimization of sodium sulphate amount, temperature and holding time can lead the development of effective technology of iron extraction from red mud by solid–phase carbothermic reduction.

Keywords: red mud, solid–phase carbothermic reduction, sodium sulphate.

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According to estimates [1], Russia has accumulated about 600 million tons of red mud – Bayer’s method alumina production waste, and each year its amount increases by additional 5–8 million tons. This waste contains a significant amount of iron, aluminum, titanium, calcium, silicon, scandium and yttrium. Currently, Russian industry processes only a small amount of the total accumulated red mud.

An active search for red mud recycling ways are stimulated not only by the potential of expanding the resource potential for the obtaining of the mentioned metals, but also the intent to solve a series of environmental problems associated with its storage. Along with valuable components, red mud contains some impurities such as sodium, chromium, and arsenic, which are potentially dangerous for the environment [2].

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The basic component of red mud is iron, which content in it can reach 40% or more. Attempts to produce iron from red mud using methods of reduction smelting [3–5], leaching [6], and direct separation in a high–intensity magnetic field [7] are well known. Magnetic separation after solid–phase carbothermic reduction of red mud can be a more promising method of iron extraction. In this method, hematite and goethite, which are the basic iron–containing minerals in red mud, are reduced by carbon–containing materials with the production of magnetite at 600–800°C [8] or metallic iron [9] at temperatures above 1100 °C. The main disadvantage of such approach is the low recovery of iron by magnetic separation and low iron grade of the obtained concentrate that is subsequence of difficulties in the separation of the reduced magnetic phases because of too small sizes of the particles. As demonstrated in further works [10–12], the use of sodium carbonate and sulphates additives during the reduction of red mud with the production of metallic iron at 1050–1150°C increases the degree of iron recovery into concentrate up to 90–95%. As a result, it is possible to produce a marketable product containing 90–95% iron with a metallization degree of more than 90%. These results were demonstrated due to the significant growth of iron grains during the carbothermic reduction in the presence of sodium salts.

In this research, we study the effect of sodium sulphate additives on the reduction of iron–containing phases and on the iron grain growth during solid–phase carbothermic reduction of red mud. We also present hypotheses regarding the mechanism of sodium sulphate influence on the growth of reduced iron grains.

In the experiments, we used red mud from Ural Aluminum Plant, from which alkali was removed by lime milk pretreatment. Table 1 presents the chemical composition of the red mud.

TABLE 1: The chemical composition of red mud, %.

Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	CaO	Na ₂ O	TiO ₂	MgO	P	S
36.9	11.8	8.71	23.8	0.27	3.54	1.01	0.42	0.14

Table 1 shows that red mud contains more than 35% of iron in terms of hematite, and also a significant amount of titanium and aluminum, which can be extracted from red mud after iron separation by hydrometallurgical methods [12]. According to the X–ray Diffraction and Mössbauer analysis, the basic red mud iron–containing minerals are hematite (α -Fe₂O₃) and goethite (α -FeOOH). The presence of a small amount of pseudobrookite (Fe₂TiO₅) is also possible.

A series of experiments was carried out to study the effect of sodium sulphate additives on the process of iron reduction and the growth of its grains during the carbothermic reduction of dealkalized red mud. Red mud with Na₂SO₄ additives in the

amount of 10% and 20%, and also without additives was heated in a muffle furnace up to a temperature of 1000–1200°C in the mixture with carbon in air and held for two hours. The obtained samples were studied by Mössbauer, X-ray diffraction, optical and electron microscopic methods. The experimental procedure and analysis of results are presented in more detail in [13].

The analysis of the samples using the Mössbauer method demonstrated that the largest amount of metallic iron (about 65%) was obtained in the red mud sample reduced without sodium sulphate at a temperature of 1100°C. It was shown that sodium sulphate addition to red mud substantially has not effect on the degree of iron metallization at this temperature. Moreover, in the sample without additives, there were no reduced iron grains with sizes exceeding 40 microns. Sodium sulphate additives led to a significant growth of reduced iron grains, and the quantity of grains larger than 40 microns at 1100°C and in the presence of 10% sodium sulphate additives exceeded 62%. The increase in the amount of sodium sulphate additives up to 20% led to a decrease of the quantity of reduced iron grains larger than 40 microns to 11.8%. Figure 1 shows microphotographs of the samples obtained after the red mud reduction without additives and with 10% Na_2SO_4 at 1100°C that obviously demonstrate the difference in metallic iron grain sizes.

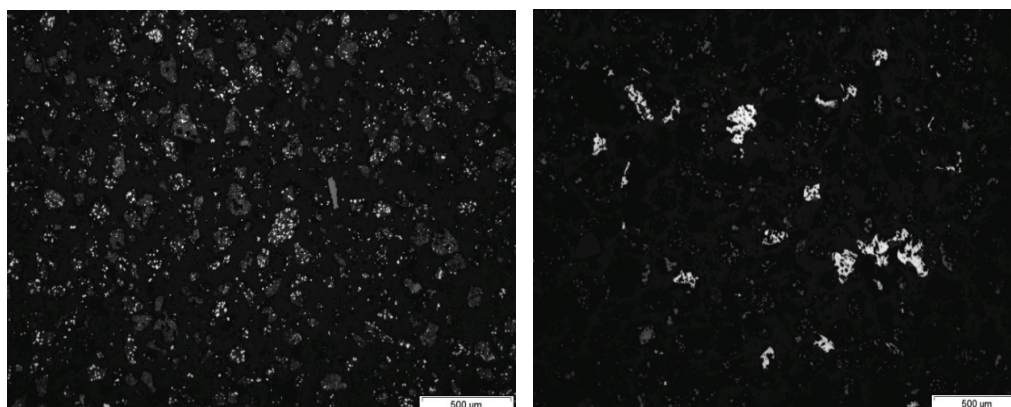


Figure 1: Microphotographs of the samples obtained after the red mud reduction (left – without additives, right – with 10% Na_2SO_4 at 1,100 °C)

With an increase in the holding temperature up to 1150°C, the size of reduced iron grains also increased, but the quantity of metallic iron decreased more than 3 times from 65% to 23% in experiments without additives, and to 21% in experiments with sodium sulphate additives. The results testify to a significant effect of sodium sulphate additives on the growth of iron grains during the red mud solid–phase carbothermic reduction, which positively influences the magnetic separation of reduced iron. Moreover, with an increase in the quantity of additive and the holding temperature, the degree of the iron reduction decreases.

Basically, the influence of sodium sulphate additives on the growth of iron grains during solid–phase reduction of various materials is connected with a decrease in the mixture melting temperature due to the reaction of sodium oxide with gangue minerals and the formation of low–melting phases [14, 15]. The emerged liquid phase leads to the agglomeration of reduced iron particles due to the acceleration of the diffusion process and the transportation of small particles to large ones. In this case, an excessive amount of the liquid phase can lead to lowering the efficiency of the iron oxides reduction due to a decrease in the diffusion of carbon monoxide in the liquid phase [16]. Some researchers [17, 18] note the possibility of the formation of a low–melting eutectic in the Fe–S system, which has a low melting temperature and reduces the surface tension of metallic iron particles, which also contributes to their agglomeration. On the other hand, this phenomenon negatively affects the metallization degree, since FeS forms before the reduction of FeO, as a result of the reaction of wustite and sodium sulphide. The iron sulphide formed on wustite particles surfaces hampers its interaction with a reducing gas, which can lead to lowering the degree of metallization. The analysis of the microstructure of reduced red mud with sodium sulphate additives at 1100°C using an electron microscope detected small FeS grains in such samples. Thus, the insufficient degree of samples metallization at 1100°C can be explained by the formation of FeS, and a sharp decrease in the amount of metallic iron at a temperature of 1150°C by an excessive amount of a liquid phase. It is possible to avoid the negative effect of sodium sulphate on the degree of iron reduction by selecting the optimum amount of its additive.

The research demonstrated the promising potential of the method of solid–phase carbothermic reduction of red mud in the presence of sodium sulphate to extract iron. It was discovered that 10% sodium sulphate additives significantly accelerate the growth of reduced iron grains, but reduce the degree of its reduction at temperatures above 1100°C.

Optimization of the amount of sodium sulphate added, temperature and holding time can lead to development of effective technologies for the solid–phase carbothermic reduction and extraction of iron from red mud.

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